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Dipolar association in binary system – acetyl acetone (HAA) in carboxylic acids

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Abstracts : Dielectric constant of binary mixtures of acetyl acetone (HAA) with butyric acid, propionic acid and acetic acid has been measured at temperature 303.16 K and frequency 455 kHz. The data of dielectric constant has been utilised to evaluate mutual correlation factor, excess molar polarization and excess Gibbs free energy to elucidate the molecular interaction. The study reveals that interaction is maximum in butyric acid + HAA system and microheterogeneous β-clusters with antiparallel orientation of dissimilar molecules predominate in it.

Keywords : Dielectric constant, binary mixture, Winkelmann Quitzsch equation

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We have already studied [1–3] the molecular interaction of acetyl acetone (HAA) with various polar and non-polar liquids with a view to identify an efficient modifier to be used for extraction of metal in nuclear energy industry. The study of HAA has been motivated in view of its ascending importance as an extractant [4]. The basis of extraction using HAA rests on separation of an organic phase from aqueous phase which however, gets complicated with the appearance of third mixed phase [5]. Hence, the need of diluent (modifier) is to be added to HAA to eliminate the third phase by improving the solvation of extracted species.

Our earlier study [2,3] indicated *p*-xylene, toluene to be more efficient as a modifier. There is evidence in the literature that iso-decanol, primary decyl-alcohol, tridecylalcohol 2-ethylhexanol *etc* [6] are used as modifier. In the present study we intend to use dielectric method to investigate the molecular interaction between HAA and carboxylic acid namely, butyric acid, propionic acid and acetic acid which might throw some light on their suitability to be used as modifier. Acetyl acetone (HAA) is a mildly associated liquid (linear correlation factor $g = 1.56$) where the intramolecular association between different HAA molecules result mostly in α-multimers [2] due to parallel alignment. But in the binary mixtures involving two polar liquids, the intermolecular association between the unlike molecules result in clusters containing molecules of both varieties. Winkelmann and Quitzsch developed a relation [7] for mutual correlation factor g_{ab} to express the short range specific dipolar interaction between dissimilar molecules. Several wokrers [8,9] have evaluated g_{ab} in polar-polar mixtures using this equation. Predominance of microheterogeneous α-clusters having parallel orientation of unlike molecules is indicated with $g_{ab} > 1$, while for the mixture, $g_{ab} < 1$, micro heterogeneous β-clusters with anti-parallel orientation are in excess.

Considering both long range and short range dipolar interaction between identical as well as dissimilar molecules in binary mixtures, Winkelmann and Quitzsch [7] developed a relation linking the permittivity of binary mixtures with those of the components in the mixtures as [7]

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$$\varepsilon_m - 1 = \sum_{r=a,b} \frac{3X_r V_r(\varepsilon_{\infty r} - 1)}{2\varepsilon_m + \varepsilon_\infty} + \sum_{r=a,b} \left(\frac{\varepsilon_{\infty r} + 2}{2\varepsilon_m + \varepsilon_{\infty r}} \right)^2 (2\varepsilon_m + 1) \frac{4\pi N}{9kT} X_r \mu_r^2 g_{rr} + \frac{(\varepsilon_{\infty a} + 2)(\varepsilon_{\infty b} + 2)(2\varepsilon_m + 1)}{(2\varepsilon_m + \varepsilon_{\infty a})(2\varepsilon_m + \varepsilon_{\infty b})} \frac{4\pi N}{9kT} (g_{ab} - 1)\mu_a \mu_b, \quad (1)$$

where a and b refer to the molecule of variety a and b, X_r denotes the respective mole fraction of the component in the mixture, ε_m is the dielectric constant of the mixture. V_r and V_m denote the molar volumes of the components and the mixture respectively, N is the Avogadros' number, K is the Boltzmann constant, T denotes temperature (Kelvin), μ_r denotes the gas phase dipole moment of the component, $\varepsilon_{\infty r}$ is taken as the square of the refractive index of the component. g_{rr} refers to linear correlation factor between identical molecules, g_{ab} is the mutual correlation factor between dissimilar molecules.

The excess molar polarization ΔP and excess Gibb's free-energy ΔG of mixing have been calculated from the equation used earlier by author [9].

The chemicals used were of anal grade purified by standard procedure [10,11] and redistilled before use.

The experimental arrangement used for the measurement of relative permittivity, *etc* is the same as used earlier by Swain [12]. The relative permittivity measurement for pure liquids as well as for mixtures was carried out by wavemeter-oscillator combination at 455 kHz [2]. The device was standardized with the help of standard liquid of known relative permittivity [13]. The cell temperature was controlled with the electronically regulated thermostatic arrangement with temperature variation of ±0.1°C. The refractive index was measured at the regulated temperature by Pulfrich refractometer at the sodium D-line. The density was measured using pycnometer of 25 cm^3 capacity. The reproducibility of relative permittivity is ±0.003 and those of refractive index and density measurements are ±0.00002 and ±0.00002 g cm^{-3}, respectively, at the temperature 303.16 K.

The dielectric constant of binary mixtures of HAA with acetic acid, butyric acid and propionic acid was measured at regulated temperature 303.16 K and frequency 455 kHz over entire range of composition. The experimental data are used to evaluate the values of g_{ab}, ΔP and ΔG_{ab} in these mixture. Some of the relevant trends are displayed graphically in Figures 1–3 and presented in Table 1.

The trend of variation of mutual correlation factor g_{ab} shows that it is less than unity throughout for mixture

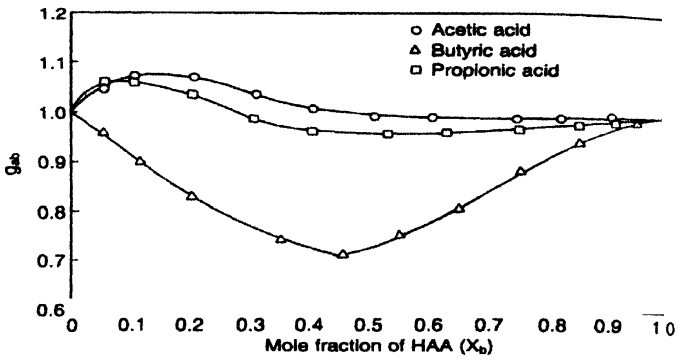

Figure 1. Variation of g_{ab} with mole fraction of HAA.

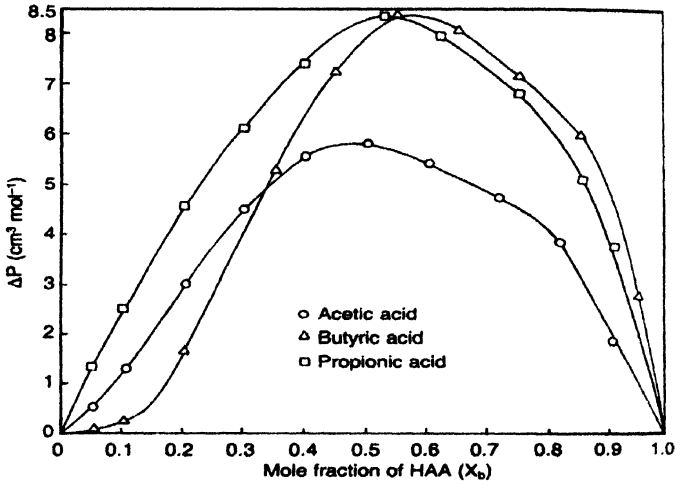

Figure 2. Variation of ΔP with mole fraction of HAA.

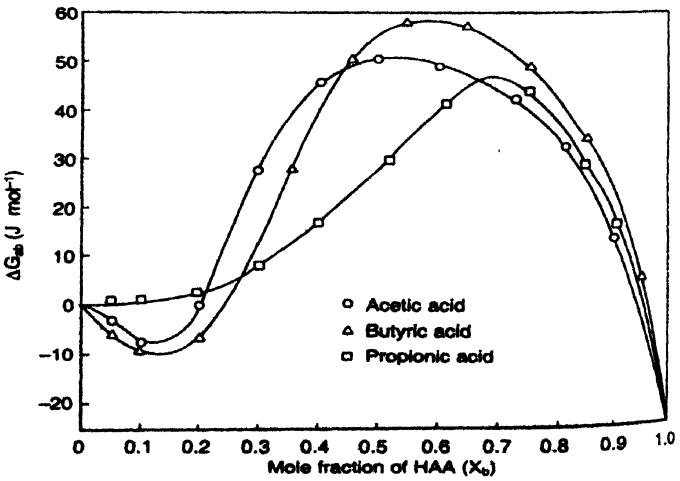

Figure 3. Variation of ΔG_{ab} with mole fraction of HAA.

Table 1. Variation of ϵ_m, g_{ab}, ΔP, ΔG_{ab} with content of HAA in acetic acid, butyric acid and propionic acid at 303.16 K.

X_h	ϵ_m	g_{ab}	ΔP (cm^3 mol^{-1})	ΔG_{ab} (J mol^{-1})
		Acetic acid		
0.05	8.00	1.050	0.50	−3.30
0.10	9.40	1.070	1.25	−7.50
0.20	11.30	1.070	3.00	2.00
0.30	13.20	1 040	4.50	27.50
0.40	15.20	1.000	5.50	45.00
0.50	17.00	0.990	5.75	50.00
0.60	18.50	0.980	5.40	48 00
0.73	20.40	0.985	4.75	42.50
0.82	22.00	0.988	3.90	32.50
0.90	23.50	0.990	1.90	14.00
		Butyric acid		
0.050	3.66	0.950	0.15	6.00
0.100	4.40	0.900	0.50	−10.00
0.200	6.40	0.830	1.65	6.00
0.350	9.00	0.750	5.25	27.50
0.450	11.00	0.710	7.25	50.00
0.550	13.20	0.750	8.25	57.50
0.650	16.00	0.800	8.00	56.20
0.750	18.00	0.875	7.15	56.00
0.850	20.40	0.935	6.00	35.00
0.950	23.00	0.985	2.75	5.00
		Propionic acid		
0.560	5.00	1.050	1.25	2.50
0.100	6.25	1.050	2.50	3.50
0.200	8.20	1.040	4.50	4.50
0.300	10.50	0.990	6 15	8.00
0.400	12.58	0.960	7.50	17.00
0.520	14.60	0.952	8.30	30.00
0.620	17.00	0.962	8.00	41.50
0.750	19.00	0.972	6.75	44.20
0.850	21.50	0.980	5.15	29.00
0.910	23.00	0.982	3.75	17.00

with butyric acid, with maximum in nearly equimolar concentration range. It indicates predominance of β-clusters of HAA-butyric acid molecules. Similar type of response have also been observed in binary mixture of methyl-isobutyl ketone (MIBK) with butyric acid [14]. On the other hand, in other two cases, g_{ab} is initially more than unity in HAA-deficient region and reduces to less than unity with increasing concentration of HAA molecules. Hence, the initial predominance of α-clusters gradually gives way to β-clusters.

The point of inflexion of g_{ab} *vs* concentration curve for the mixture with butyric acid, is rather sharp while in other mixtures, it is relatively shallow. It probably indicates greater efficacy of butyric acid as a modifier.

The HAA molecules can exist both in keto and enol-form [2]. In pure form, acetyl acetone has wood-pile structure due to intramolecular association between $C^{\delta+}$ and $O^{\delta-}$ resulting in α-multimers while it results in α-multimers in haed-tail configuration in enol form. The g value in pure liquid being 1.56, indicates the predominance of wood-pile arrangement in it. On the other hand, the acid molecules have closed ring structures resulting in β-multimers with g less than unity.

On addition of HAA in acid, it is likely that the intramolecular bonds in the individual constituents will break and some of the dissimilar molecules will enter into the intermolecular associtation, the acid acting as a proton donor. It is possible that association may result either in α-clusters or in β-clusters. The former necessitates a strained linkage while latter needs head tail linkage which is relatively stable. In butyric acid, the intramolecular bonds are relatively strong as evidenced by very low value of g. As such it is probable that there will be tendency of formation of relatively stable linkage resulting in β-clusters over the entire range. On the other hand, in acetic acid and propionic acid, the value of g is relatively high and hence the bonds are correspondingly weak. Hence, it is possible that initially the effect of HAA molecule predominates and small number of true acid molecules provide strained linkage due to switching mechanisms [15,16] resulting in more α-clusters.

The nature of variation of ΔP also supports our earlier conclusion in as much as the occurrence of maximum in ΔP and point of inflexion in the curve g_{ab} *versus* mole fraction do almost coincide. The magnitude of ΔP being maximum for butyric acid at same concentration for which g_{ab} departs most from unity.

The trend of variation of ΔG_{ab} complements our conclusion drawn from study of g_{ab} and ΔP. In all systems, it has low negative value in HAA-deficient region while it is positive in the rest. β-clusters characterised by reduced internal energy are expected to make the excess free energy positive. Hence, formation of β-clusters are expected to result in increase in free-energy of the system.

The maximum (+ve) of ΔG_{ab} in butyric acid system coincides with the minimum (−ve) value of g_{ab} in the process of formation of β-clusters. The low (−ve) value

of ΔG_{ab} in butyric acid system may be due to limitations of the theoretical equation whereas the negative value in the other two system coincides with the region where α-multimers are predominant.

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